EXTERNAL PEER REVIEW OF THE SCIENTIFIC BASIS OF THE PROPOSED BASIN PLAN AMENDMENT TO ESTABLISH CONTROL OF PYRETHROID PESTICIDES DISCHARGES IN THE SACRAMENTO AND SAN JOAQUIN RIVER BASINS

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Charge to Reviewers

It is the reviewer's responsibility to determine whether the scientific portion of the proposed rule is based upon sound scientific knowledge, methods, and practices. The proposed rule is the Draft Basin Plan Amendment (Appendix A in the Draft Staff Report). Scientific peer reviewers should make this determination for each of the identified assumptions, findings, and conclusions that constitute the scientific portions of the Draft Basin Plan Amendment and that is listed below.

Pyrethroid Pesticides Water Quality Objectives

1. ***The proposed water quality objectives are protective of the beneficial use(s) that is most sensitive to pyrethroid pesticides. The Draft Staff Report evaluates several potential water quality objectives and concludes that the acute and chronic water quality criteria derived in 2015 using the University of California - Davis methodology, are scientifically sound and are protective of beneficial uses.***

Review: The staff report identifies warm and/or cold aquatic life habitats as the beneficial uses most sensitive to impairment by pyrethroid insecticides in either water or sediment. The basis of this conclusion is that pyrethroid insecticides are reported in the scientific literature to have the highest toxicity to aquatic and sediment dwelling arthropods. The conclusions of the staff report appear to be well founded in cited literature as well as consistent with the general scientific consensus I have heard over the years in professional and regulatory meetings regarding pyrethroids. The UC Davis method that established 2015 acute and chronic water quality criteria is a logical basis for water quality objectives for these compounds as it allows the calculation of numeric standards for each of the pesticides of interest and should be low enough to be protective of the beneficial uses. I concur that the other alternative methods presented would not be as protective for beneficial uses as they had higher numeric values or were designed such that numeric values could not be developed for some of the pyrethroid insecticides of interest due to the lack of data. In many respects the UC Davis method is consistent with and mirrors the US EPA method for developing criteria but allows greater flexibility to handle data sets and the development of numeric values when full data sets required for the EPA method are not available.

Pyrethroid Pesticides Water Quality Criteria Derivation Methodology

2. ***The underlying method for deriving the proposed pyrethroid pesticides water quality criteria, which are proposed as water quality objectives and TMDLs, is scientifically***

sound. The UC-Davis Methodology and the criteria derived by this method are technically valid and scientifically sound for use as water quality objectives and TMDLs. The following procedures result in conservative criteria that are scientifically sound and protective of sensitive species, and are not overly conservative:

2A. The UC-Davis Methodology uses 24-96-hour toxicity data to derive acute criteria not to be exceeded over a 1-hour averaging period and longer duration chronic toxicity data to derive chronic criteria not to be exceeded over a 4-day averaging period. In addition, the most sensitive life-stage and endpoint are used among toxicity data for a given species. The use of toxicity data from longer durations than the criteria averaging period does provide conservatism to the criteria; based on scientific evidence this is valid in order to ensure that the values are protective of all species in an aquatic ecosystem, including those for which no toxicity data is available.

Review: The criteria developed using the UC Davis method are attained if the averaging periods do not exceed the chronic criteria more then once every three years. This longer duration should be protective and is appropriate given the current state of the science. As stated in the staff report, the criteria are based upon toxicity to the most sensitive species tested, in this case, *Hyalella azteca* which notably was consistently the most sensitive species in all tests. However data was also presented in the staff report that there is evidence native (ie wild) populations of *Hyalella* do adapt to develop resistance to chronic low-level amounts of pyrethroids over time, thus laboratory based-toxicity assessments using laboratory reared organisms, and the corresponding criteria based upon them, may overestimate the potential impact on the same species in the field. While the current status of data at this point would not justify a higher criteria value, it may in the future as the database in the research of native species evolution and "ruggedness to chemical insult" continues to evolve and expand.

2B. The authors recommend using the lower 95% confidence interval of the 5th percentile or the 1st percentile of the SSD for downward adjustment of criteria. Five of the six 2015 water quality criteria derived using the UC-Davis Methodology were adjusted downward using the 1st percentile of the SSD to be protective of sensitive species in the data sets, however, using the 5th percentile would be more consistent with other methodologies.

Review: The downward adjustment of the criteria for bifenthrin, cyfluthrin, cypermethrin, esfenvalerate and lambda-cyhalothrin using the 1st percentile of SSD is scientifically sound based upon the UC Davis method and consistent with stated policy to provide the greatest degree of protection to the most sensitive species. In general, the major differences between using the 5th percentile vs the 1st percentile of the SSD results in an approximate order of magnitude difference in criteria values. A great deal of conservatism is already built into the process via a maximum exceedence of the chronic criteria of once over 3 years over a 4 day averaging period and using toxicity values based upon laboratory reared organisms that appear to be more sensitive then native organisms in impacted waters. While use of the 1st percentile of the SSD is consistent with scientific knowledge, methods and practices it would appear to be overly protective

based upon the conservatism already in place. Criteria values based upon the 5th percentile would be equally justified scientifically, consistent with other national and international methods and standards as noted by the staff report, and would likely still provide adequate protection for the identified beneficial uses.

2C. It is scientifically sound to mix flow-through, static renewal, and static data in deriving criteria and does not introduce bias that would lead to criteria that are underprotective or overly conservative. While data from flow-through tests based on measured concentrations is preferred, using the best available data for a given species is technically valid.

Review: It is an acceptable scientific practice to mix data collected from flow-through, static renewal and static toxicity studies for criteria development as long as there are established metrics that dictate acceptable data quality that are applied consistently to each study. The UC Davis method uses a processes that applies metrics in study evaluation, and a ranking system for selection of one study type over another (e.g. flow-through vs static; measured concentrations are preferred over nominal concentrations, etc). Studies selected for criteria development are ranked according to both relevancy and reliability and are given designations of RR (Relevant and Reliable). Studies rated as less reliable in either category are used as supplemental information. Studies rated as unreliable are not used to develop criteria.

2D. ***When there are insufficient acute toxicity data to use a species sensitivity distribution to derive the acute criterion, the UC Davis methodology Phase II Report includes assessment factors that are applied to the lowest acute toxicity value in the data set in order to estimate the 5th percentile of a distribution. The assessment factors decrease as the number of available data increase because uncertainty decreases with increasing information. The assessment factors were derived by a mathematical procedure from the USEPA guidance for the Great Lakes system using existing high quality pesticide data sets. It is recognized that assessment factors are a conservative approach for deriving water quality criteria, but when little data is available; it is scientifically sound to use a conservative approach. Similarly, the UC Davis methodology Phase II Report provides a default acute-to-chronic ratio to use for derivation of chronic criteria when too few chronic toxicity data are available to derive criteria using a species sensitivity distribution or empirical acute-to-chronic ratios for the pesticide of interest. The default acute-to-chronic ratio is based on the 80th percentile of available empirical acute-to-chronic ratios for other pesticides, following the US EPA guidance for the Great Lakes system. Use of the 80th percentile provides some conservatism to the default acute-to-chronic ratio, which is scientifically sound to account for the uncertainty in using this value for pesticides for which little to no chronic toxicity data are available.***

Review: The use of assessment factors and also default acute-to-chronic ratios for other pesticide classes to develop criteria, while not ideal, are still scientifically sound and acceptable in the absence of high quality data for the pesticides of interest. The UC Davis method directly follows EPA guidance in this manner and thus has an established

proven precedent. Ideally, the other pesticide data sets chosen would be those that are within the same class of pesticide (ie. In this case another pyrethroid). In the absence of this, pesticides chosen with the same mode of action would be a secondary selection factor.

Additive Toxicity of Pyrethroid Pesticides

3. For determining attainment of water quality objectives it is scientifically sound to consider the six pyrethroid pesticides additively if more than one is detected in a water sample. Based on current information available, it is not scientifically sound to assume additive toxicity of other constituents with pyrethroid pesticides.

Review: It is scientifically sound and consistent with regulatory practice to consider the six pyrethroids additively as all have the same mode of action. It is reasonable to assume that if multiple compounds are detected in a water or sediment sample, any organism in contact with that media would be equally exposed to all of them, and they would behave additively if they have the same mode of action. This is a similar approach that has been used for organophosphate and carbamate insecticides and is the basis of aggregate risk assessment under the Food Quality Protection Act of 1996, used to assess human health risk of exposure to multiple pesticides with similar modes of action across all media. In the case of pyrethroid insecticides, there is an adequate literature base to establish a line of evidence that they do indeed act additively as a mixture. It is very likely that other classes of chemicals present in impaired waters will also act additively, especially those with a neurochemical mode of action (e.g. metals, antidepressant pharmaceuticals such as sertraline). However at this junction there is not an adequate literature basis to justify including these or other chemicals and thus I concur with the staff assessment that it is not scientifically sound to assume additivity with other constituents.

Bioavailability and Compliance Determination

4. For determining attainment of water quality objectives, it is scientifically sound to use the measured or estimated freely dissolved aqueous concentrations of pyrethroid pesticides. The proposed equation to estimate freely dissolved concentrations and the default partition coefficients are scientifically sound and protective of beneficial uses.

Review: There is a well-established literature basis to show that pyrethroid insecticides associate mostly with sediment and dissolved organic matter in water. In the particulate phase it is highly unlikely pyrethroids are bioavailable to aquatic organisms and the literature basis for this conclusion is relatively clear. The literature basis is not as strong to make the case that pyrethroids are not bioavailable when associated with dissolved organic matter (or dissolved organic carbon), however the literature does indicate bioavailability is significantly reduced in the presence of increasing levels of DOC/DOM. The most conservative approach would be to use whole water concentrations for attainment assessment however this would likely be overly conservative and grossly overestimate exposure. As discussed above there is already a large degree of conservatism (and therefore implicit safety) designed into the UC Davis method, thus the use of freely dissolved concentrations are appropriate, the most scientifically justified and should result in adequate protection of beneficial uses. The proposed equation to

estimate freely dissolved concentrations is also scientifically sound. The default partition coefficients are also reasonable and scientifically sound to use. Attempting to collect site-specific partition coefficients is unreasonable as these are likely to be highly variable both spatially and temporally and ultimately would have a have a negligible change on the values determined in surface water to assess attainment, especially given the uncertainty introduced and associated with analytical measurements at sub part-per-trillion concentrations (see discussion below in section 5 and "the Big Picture, part (b)").

Pyrethroid Pesticides TMDLs

5. The proposed TMDL loading capacity, allocations, margin of safety, and numeric targets are clearly described and consistent with attaining water quality objectives that are protective of the beneficial use(s) most sensitive to pyrethroid pesticides.

Review: The staff recommendation is that the TMDL loading capacity be concentration-based equal to the water quality objectives. These are established using the additive formulas used to calculate criteria-normalized concentration units. These concentration-based loading capacities would equate to wasteload allocations applicable only to the two storm-water systems stated in the report but presumably could be expanded to others as well. As these storm water systems are the only sources and there are no non-point sources in listed waterbodies within these systems, no load allocations are proposed. As the numeric criteria form the basis of all loads and subsequent allocations, which in turn are based upon the UC Davis method, these should be adequately protective of beneficial uses. Ultimately attainment will be based upon collection of adequate data to do the calculations, presumably from water-monitoring.

Unfortunately adequate methods to monitor pyrethroids consistently and accurately at the concentrations approaching criteria levels do not exist at this point in time. As analytical detection limits are higher then criteria levels any detection would constitute non-attainment, and non-detection would not necessarily guarantee attainment of criteria. Sediment toxicity testing is also proposed, presumably with the most sensitive species, *Hayella azteca* as a possible indication of the presence of pyrethroids, however due to the low levels of pyrethroids that can cause toxicity and the lack of analytical methods sensitive enough to reliably confirm the presence of pyrethroids at these levels, it is hard to imagine how meaningful results would be obtained from any monitoring efforts. This issue is acknowledged in later chapters (Implementation and Monitoring) of the Staff report as well as in the Basin Plan Amendment itself. In these chapters and the Basin Plan Amendment adequate flexibility to address these issues on a case-by-case basis appear to be in place.

The Big Picture

(a) In reading the Draft Staff Report and Draft Basin Plan Amendment language, are there any additional scientific issues that should be part of the scientific portion of the proposed rule that are not described above? If so, comment with respect to the Draft Staff Report and Draft Basin Plan Amendment.

Review: The Draft Staff Report as well as the Draft Basin Plan Amendment are very well-written and comprehensive in scope. The report, assessments and conclusions are

based upon state of the art science, as it exists to date. The authors are thorough in their evaluation of the scientific uncertainties that undoubtedly exist that could impact the assessment and corresponding criteria calculations. Examples of these uncertainties are additive toxicity associated with other contaminants possibly with similar or dissimilar modes of action, the existence of native *Hayella* population evolutionary pyrethroid resistance likely due to chronic exposure, and bioavailability of pyrethroid residues sorbed to sediment or associated with dissolved organic matter/organic carbon. The authors clearly explain why these were addressed or not addressed in assessments and provided a current literature basis to support their conclusions. I have no other substantive comments to add in this area.

(b) Taken as a whole, is the scientific portion of the proposed actions based upon sound scientific knowledge, methods, and practices?

Review: The proposed actions are based upon sound science considering only the criteria and on the basis of toxicity. However taken as a whole one cannot realistically ignore that the proposed criteria are well below the range that pyrethroid insecticides can be reliably measured in water and sediment samples for monitoring and subsequent enforcement activities. Most of the methods referenced in the papers where monitoring data were reported, and many in the referenced toxicity studies were based upon electron capture detector (ECD) methods using two-column confirmation. While this is considered an acceptable practice it is still highly prone to error especially in difficult environmental matrices as it is non-selective and not based upon structural features of the analyte. Typically the quality control demands require much higher signal-to-noise ratios to definitively state an analyte is indeed present in the matrix, and this needs to be addressed on a chromatogram-by-chromatogram basis. The papers that were referenced and monitoring data presented did not include the chromatograms or quality assurance data supporting QC criteria (as is typical in most published studies) so I am left to presume that the referenced paper's authors used expert judgment in assigning detections and their data analysis is correct. Example chromatograms supporting the Appendix C data set (Weston and Lydy, 2010) would have been useful. The challenges in detection of analytes was addressed by the Draft Report authors briefly in the monitoring section of this report however I felt this could have been more heavily reviewed and discussed further. Current research is indicating that gas chromatography coupled with triple quadrupole mass spectrometry methods incorporating negative chemical ionization (GC/MS/MS – NCI) have promise to reaching lower levels of detection, however further work will be needed in these areas. Given the amount of time before compliance will be required it is likely that sensitive methods will be available as the criteria in these reports will set the need and threshold of required analytical detection limits necessary for monitoring and complience.

As mentioned earlier, this issue was acknowledged in both the Draft Staff Report and in the Basin Plan Amendment itself, and engagement and discussion was recommended between both the water-board and regulated entities before initiating any monitoring effort. Given the uncertainties currently existing in methods to reliably measure these analytes, the proposed actions are based upon sound scientific knowledge and practices.